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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE  
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES**

Inventor/Appellant: Partho Sarkar

Title: CRACK-RESISTANT ANODE-SUPPORTED FUEL CELL

Application No. 10/658,803

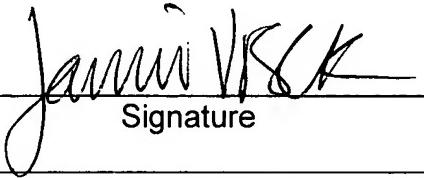
Filed: September 9, 2003

Examiner/Art Unit: ALEJANDRO, Raymond / 1745

Attorney File No.: 2281-001-03

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**APPEAL BRIEF**

Dear Commissioner for Patents:

This is an appeal pursuant to 37 C.F.R. § 1.191(a) from the decision of the Examiner, dated June 5, 2006, finally rejecting claims 1-12 of the above-referenced patent application. A request for a one-month extension of time is enclosed pursuant to 37 C.F.R 1.36(a).

Attached to this Brief as **Appendix A** is a claims appendix containing a copy of all the claims involved in the Appeal, as required under 37 C.F.R. §41.37(a)(viii). An evidence appendix as required under 37 C.F.R. §41.37(a)(ix) accompanies this Brief in the form of **Appendices B-E**. **Appendix B** contains pages from a publication that illustrates the oxygen ion conduction and high electrical conductivity characteristics of the solid electrolyte yttria stabilized zirconia ("YSZ") that make YSZ suitable for use in

the anode support layer of a solid oxide fuel cell ("SOFC"). **Appendix C** contains pages from a publication illustrating the relatively high electrical resistivity of alumina (aluminum oxide). **Appendix D** contains pages from a publication further discussing desirable characteristics of solid electrolytes suitable for use in SOFCs. **Appendix E** lists several Web sites that contain exemplary information illustrating the characterization and use of alumina as an insulator.

The objective evidence that accompanies this brief as **Appendices B-E** was made of record in the Response to final Office Action filed on October 11, 2006. This evidence was submitted after the final Office Action because this was when the Examiner first requested such evidence (See page of the Interview Summary mailed September 12, 2006). Thus, this evidence was necessary to fully respond to the Examiner's request and could not have been earlier presented since such a request had not been made until that point in the prosecution of the present application. These are certainly good and sufficient reasons pursuant to 37 C.F.R. § 1.116(e) and this evidence is therefore of record in the present application in accordance with 37 C.F.R. §41.37(c)(2).

A related proceedings appendix as required under 37 C.F.R. §41.37(c)(1)(ii) accompanies this brief as **Appendix F** and indicates there are no related appeals, interferences, or judicial proceedings, as is discussed in more detail in Section II below.

## I. *Real Party In Interest*

The real party in interest is Alberta Research Council, Inc., having a principal place of business at 250 Karl Clark Road, Edmonton, Alberta T6N 1E4, Canada. The inventors assigned this application to Alberta Research Council, Inc. ("Assignee") in an Assignment recorded on February 9, 2004 at reel no. 014958, frame no. 0347.

## II. *Related Appeals and Interferences*

Based on information obtained from Alberta Research Council, Inc., and based on information and belief of the undersigned attorney, there are no prior or pending

appeals, interferences, or judicial proceedings known to Appellant, Appellant's legal representative the undersigned attorney, or the Assignee, which are related to, which directly affect or which will be directly affected by, or which have a bearing on the decision of the Board of Patent Appeals and Interferences ("the Board") in the pending Appeal. There are no such appeals, interferences, or judicial proceedings as indicated in the related proceedings appendix that accompanies this brief as **Appendix F**.

### **III. *Status of the Claims***

Claims 1-13 are pending and stand rejected by the Examiner. Claims 1-12 are appealed.

### **IV. *Status of Amendments***

An Amendment After Final was filed on October 11, 2006 in response to a Final Office Action mailed on June 5, 2006. In an Advisory Action mailed on October 17, 2006, the Examiner indicated the proposed amendments in the Amendment After Final would not be entered as raising new issues that would require further consideration and/or search. **Appendix A** includes all the appealed claims 1-12 as they are currently pending.

### **V. *Summary of the Invention***

This summary of the invention provides cross-referencing to the application as required by 37 C.F.R. § 41.37(c)(v). This cross-referencing is solely to assist the Board in understanding the Applicant's invention and is not meant to be exhaustive or to limit the scope of the pending claims.

Independent claim 1 recites an anode-supported solid oxide fuel cell including an anode support layer comprising a porous ion-conducting structure having pores impregnated with a catalytic and electronically conductive material. An electrolyte layer is in adjacent intimate contact with the anode support layer and a cathode layer is in adjacent intimate contact with the electrolyte layer. Figure 1 illustrates a planar anode-

supported solid oxide fuel cell 2 corresponding to one embodiment of invention covered by claim 1. The fuel cell 2 has a number of layers 10-18 in contiguous intimate contact, namely a cathode layer 10, an electrolyte layer 12, an anode functional layer (AFL) 14, an anode support layer 16 (ASL), and a pair of metallic current collectors 18 sandwiching these layers 10, 12, 14, 16. See paragraph 16. The current collectors 18 would typically be electrically coupled to an external circuit (not shown) to transmit electrons produced during the electrochemical reaction of the fuel cell 2.

As described in paragraph 18, the cathode layer 10 may be composed of magnesium doped lanthanum manganate (LaMnO<sub>3</sub>) or a lanthanum strontium manganate (LSM), the electrolyte layer 12 made of a fully dense (*i.e.*, non-porous) yttria-stabilized zirconia (YSZ), which is an excellent conductor of negatively charged oxygen ions at high temperatures, and the anode functional layer 14 composed of porous nickel / zirconia cermet material. See paragraph 18. The ASL 16 is composed of a solid state YSZ structure impregnated with Ni or Ni-containing compounds. Other catalytic and electrically conductive materials may be substituted for the Ni or Ni-containing compounds. *Id.* The same is true of the YSZ structure, with other oxygen ion conducting materials suitable for SOFC use and having a relatively similar thermal coefficient to the electrolyte being substituted for YSZ. *Id.*

The ASL 16 is a porous ion-conducting structure having pores impregnated with a catalytic and electronically conductive material. The ASL 16 may be produced by sintering a powder containing YSZ and combustible additives at a temperature sufficient to enable the YSZ to achieve partial densification in a solid state and to burn out the combustible additives. Paragraph 19, line 7 *et seq.* The porosity is provided by way of interconnected pores formed as a result of the combustion of the sintering additives, with the target porosity of the ASL 16 being on the order of about 30% or greater. *Id.* After forming the porous YSZ ASL structure, the pores of the YSZ ASL structure are impregnated with nickel Ni or a nickel compound. This impregnation is then followed by heat treatment steps that are typically made in both oxidizing and reducing atmospheres, which causes the impregnated nickel to typically be in both metallic (Ni) and oxide (NiO) form. *Id.*

The impregnation process is carried out such that Ni/NiO is distributed thoroughly throughout the porous YSZ ASL structure in a sufficient quantity (below 75% of the pore volume, and typically below 50% of the pore volume) that, upon heat treatment, the Ni-phase is continuous through the inside of the YSZ ASL porous structure. See paragraph 20. This continuous distribution of Ni provides an electronic current path that enables the ASL 16 to serve as a current collector. After final heat treatment, Ni/NiO does not completely fill the pores in the YSZ ASL structure since the pores need to remain open to provide reactant gas passage through the ASL 16. *Id.*

As set forth in paragraph 21, during operation of the solid oxide fuel cell 2 fuel is supplied to and permeates through the ASL 16 and is oxidized to produce electrons. Under certain circumstances, such as when an insufficient amount of fuel is supplied for the electrochemical reaction ("fuel starvation"), the nickel Ni in the ASL 16 may oxidize to thereby form NiO. Paragraph 21, lines 2-4. Since NiO has a different density than Ni, its formation will cause a volume change relative to Ni. Paragraph 21, line 5 *et seq.* The Ni/NiO of the ASL 16 is, however, impregnated inside the porous YSZ ASL structure. *Id.* As a result, since the expected volume change associated with the oxidation of the Ni to NiO of the YSZ ASL structure is less than the volume of the pores in this structure, it is expected that no or minimal change in the overall volume of the ASL 16 will occur as a result of Ni oxidation. *Id.* The overall thermal expansion coefficient for the ASL 16 is also expected to be reduced as a result of using Ni-impregnated YSZ instead of a traditional zirconia-nickel cermet. *Id.*

In the ASL 16, the volume changes of this structure resulting from Ni/NiO oxidation and/or thermal expansion/contraction are expected to be less than in traditional cermet anode support layers. As a result, it is expected that the electrolyte layer 12 will experience less associated mechanical stress during operation, thereby reducing the occurrence of volume-change-induced cracking of the electrolyte layer. Although not discussed in detail, claim 1 also covers embodiments of the present invention illustrated in Figures 2-4.

Turning now to independent claim 12, this claim recites an anode-supported solid oxide fuel cell including a cathode layer in adjacent intimate contact with an

electrolyte layer that is in adjacent intimate contact with an anode functional layer. The anode functional layer is in adjacent intimate contact with an anode support layer comprising an ion-conducting structure with a plurality of vias extending through the thickness of the oxygen ion-conducting structure, with at least some of the vias being filled with electronically conductive material. Claim 12 covers, for example, the embodiment of the present invention illustrated in Figure 2. In this embodiment, the ASL 16 is provided with a plurality of vias 20 (channels) that span the thickness of the ASL 16, and provide a pathway for the flowthrough of reactant gas. Paragraph 24, lines 2-3. The vias 20 may be created by one of the known methods in the art, e.g. by hole punching, *id.* at lines 3-4, and are filled with electronically conductive materials such as Ag, Ag/Ni -alloy or any other silver alloys, Cu or Cu alloys, Ni or Ni alloys, tungsten and its alloy, and so on, to enable the ASL 16 to serve as a current collector. *Id.* at lines 5-7. The rest of the ASL 16 structure may be substantially free of Ni or another electrically conductive material such that electric current flowing from the ASL 16 to the current collecting layer 18 flows mainly through the vias 20. *Id.* at lines 7-10. Alternatively, the rest of the ASL 16 structure may be impregnated with Ni/NiO to assist in catalyzing and current conduction. *Id.* at lines 10-11.

Figure 3 illustrates the ASL 16 having a graded composition along its thickness according to another embodiment of the present invention. Figure 4 illustrates another embodiment of the present invention in which a buffer layer 22 is introduced between the AFL 14 and the ASL 16.

## VI. *Issues*

- 1. Whether U.S. Patent Application Publication No. 2002/0164523 to Shibata et al. (“Shibata”) anticipates claims 1-6, 9, and 11-12 under 35 U.S.C. § 102(e).**
  
- 2. Whether claims 7-8 and 10 are obvious under 35 U.S.C. § 103(a) in view of the combination of Shibata and U.S. Patent Application Publication No. 2002/0028367 to Sammes et al.**

(“Sammes”).

**VII. Grouping of Claims**

1. Claims 1-6, 9, 10, and 11-12 stand or fall together.
2. Claims 7 and 8 stand or fall together.

**VIII. Argument**

1. **Claims 1-6, 9, and 11-12 are allowable under 35 U.S.C. § 102(e) over U.S. Patent Application Publication No. 2002/0164523 to Shibata et al. (“Shibata”) because Shibata neither discloses nor suggests an anode support layer comprising a porous ion-conducting structure having pores impregnated with a catalytic and electronically conductive material.**

“Under 35 U.S.C. § 102, every limitation of a claim must identically appear in a single prior art reference for it to anticipate the claim.” Gechter v. Davidson, 42 USPQ2d 1030, 1032 (Fed. Cir. 1997). Before determining whether a prior art reference anticipates a claim, one must first construe the claim “to define the scope and meaning of each contested limitation.” *Id.* The proper starting place in any claim construction analysis is the claim language itself read in view of the specification and the prosecution history. *Phillips v. AWH Corp.*, 415 F.3d 1303 (Fed. Cir. 2005) (*en banc*).

In the final Office Action mailed 5 June 2006, the Examiner maintained the rejections of claims 1-6, 9, and 11-12 under 35 U.S.C. § 102(e) as being anticipated by Shibata. On September 7, 2006, the undersigned along with the inventor Partho Sarkar and Brian Y. Lee, Canadian counsel for the Assignee, held a telephone interview with the Examiner to discuss the rejections of the pending claims (See the Examiner’s Interview Summary mailed September 12, 2006 that is part of the file history of the present application). During this telephone interview, the Examiner construed the “porous ion-conducting structure having pores impregnated with a catalytic and electronically conductive material” recited in claim 1 as corresponding to the porous

metallic base body 1 illustrated in Figures 4-7. Paragraph 44 of Shibata states "it may be possible for the porous metallic base body [1] to be made of a ceramic which is plated with the above metals [e.g., nickel Ni] or with the alloy containing the above metals." Paragraph 69 more specifically provides "the porous base body 1 ... includes a ceramic (alumina) body plated with [nickel] Ni." In both the final Office Action (Item 2, bottom of page 3) and during the telephone interview, the Examiner erroneously concluded that the alumina portion of the base body 1 corresponds to the "porous ion-conducting structure" and the nickel Ni coating corresponds to the "catalytic and electronically conductive material" as recited in claim1.

Notwithstanding the Examiner's assertions, alumina is not a porous ion-conducting material. This fact is well understood and known by those skilled in the art. Alumina is an insulator having a resistivity that is too high for this material to be considered a solid electrolyte and an oxygen ion conductor suitable for use in a solid oxide fuel cell. In order for a material to be considered an oxygen ion conductor suitable for use in an electrode of a solid oxide fuel cell, the material must provide the necessary and efficient ionic path for anodic reaction which takes place during solid oxide fuel cell operation. As is well known in the solid oxide fuel cell art, the ionic conductivity of the anode must be comparable to the ionic conductivity of the electrolyte. Moreover, alumina's resistivity is too high at the operating temperature of a solid oxide fuel cell to perform the required electrode function for the fuel cell.

During the Examiner interview, the Examiner contended that even if alumina is considered in the prior art as an insulating material this material is nonetheless capable of conducting some ions, even if such ion conductivity is poor. See page 3 of the Interview Summary. The Examiner requested objective evidence to support that such an alumina ceramic is "incapable" of transporting ions, meaning that the material exhibits no ion conduction at all. *Id.*

A suitable material for the recited anode support layer and thus an ion-conducting material is yttria stabilized zirconia (YSZ). See, e.g., paragraph 8 of the present application. YSZ is an excellent conductor of negatively charged oxygen (oxide) ions at high temperatures. See paragraph 3. A solid oxide fuel cell operates at

an elevated temperature, typically on the order of between 700-1000 °C. *Id.* See page 101 of the Suresh publication that accompanies this amendment as **Appendix B** regarding general characteristics of ion-conducting materials. Other oxygen ion conducting materials suitable for use in a solid oxide fuel cell may be substituted for YSZ in the anode support layer. See paragraph 19. A characteristic of a solid electrolyte, which may otherwise be known as a fast ion conductor or a superionic solid, is a high electrical conductivity in the range of  $10^{-1}$ - $10^{-4}$  ohm $^{-1}$ xcm $^{-1}$  (*i.e.* a resistivity of 10-10,000 ohm $^{-1}$ cm $^{-1}$ ). See page 17 of **Appendix B**. In contrast, alumina (aluminum oxide) has a resistivity of  $5.0 \times 10^8$  at 700°C and  $2 \times 10^6$  at 1000°C (see page 959 of the Shackelford and Alexander publication, which accompanies this amendment as **Appendix C**. This large resistivity of alumina plainly evidences that alumina is not a solid electrolyte/fast ion conductor/superionic solid suitable for use in a solid oxide fuel cell. See the highlighted portions of the article that accompanies this amendment as **Appendix D** for additional information regarding desired resistivity values in fuel cells. **Appendix E** contains a listing of several Web sites that illustrate alumina being characterized and used as an insulator and not an ionic-conductor.

All the above evidence clearly demonstrates that the Examiner is in error in asserting that the alumina disclosed in Shibata corresponds to the recited porous ion-conducting material. Moreover, the Examiner's contention that because alumina must exhibit some ion conductivity the base body 1 of Shibata may be considered to correspond to the porous ion-conducting structure of the anode support layer recited in claim 1. Materials are classified as having physical characteristics that result in each material being placed in a particular class of materials, such as an electric or thermal conductor or insulator or an ionic conductor or insulator. Materials are not classified in absolute terms as would be required using the Examiner's logic. The Examiner requested evidence that "ceramic alumina is INCAPABLE of transporting ions (no ion conduction at all)." See page 3 of the Interview Summary. No such evidence can be provided for any material. Although classified as a particular type of material, every material will exhibit some characteristics of another class of materials. For example, materials classified as electrical insulators exhibit some amount of electrical conductivity, but such conductivity is so small that these materials are nonetheless

classified as insulators. If the Examiner's argument was accepted, then the classification of materials would be rendered meaningless. Any material could be said to be whatever type of material was needed by an Examiner when formulating a rejection.

Pursuant to MPEP § 2111, during patent examination the pending claims must be given their broadest reasonable interpretation consistent with the specification. The Examiner expressly mentioned this well known tenet of patent examination during the Examiner interview. As expressly set forth in Section 2111, the "broadest reasonable interpretation of the claims must also be consistent with the interpretation that those skilled in the art would reach." As evidenced by the accompanying technical literature, one skilled in the art would not interpret the phrase "ion-conducting structure" to include the insulating material of alumina ceramic. The Examiner's attempt to so interpret this phrase is simply put an unreasonable interpretation of this language. Although the Examiner cites the "broadest reasonable interpretation" language of Section 2111 as the rationale for his interpretation, such an interpretation of this language plainly in violation of this section of the MPEP as well as in contravention of common sense.

For all these reasons, Shibata neither discloses nor suggests an anode support layer comprising a porous ion-conducting structure having pores impregnated with a catalytic and electronically conductive material as recited in claim 1. The base body 1 of Shibata simply cannot be said to correspond to the recited anode support layer. As discussed above, an alumina ceramic simply is not "a porous ion-conducting structure." Because an alumina ceramic exhibits some ion conductivity does not make such an alumina ceramic an ion-conducting structure. As previously discussed with reference to **Appendices B-E**, alumina's resistivity is too high for this material to be considered a solid electrolyte and an ion conductor for a solid oxide fuel cell. Alumina's resistivity is also too high at the operating temperatures of solid oxide fuel cells to carry out the required electrode function.

Furthermore, claim 1 recites an electrolyte layer in intimate contact with the anode support layer. Shibata discloses electrodes 10 and 11 to be in intimate contact with the electrolyte and not the base body 1 asserted by the Examiner to correspond to

the anode support layer. Thus, claim 1 is allowable for this additional reason.

For all these reasons, the combination of elements recited in claim 1 is allowable and dependent claims 2-11 are allowable for at least the same reasons as claim 1 and due to the additional limitations added by each of these claims.

Claim 12 recites an anode-supported solid oxide fuel cell comprising an anode support layer including an ion-conducting structure with a plurality of vias extending through the thickness of the oxygen ion-conducting structure. At least some of the vias are filled with electronically conductive material. An anode functional layer is in adjacent intimate contact with the anode support layer and an electrolyte layer is in adjacent intimate contact with the anode functional layer. A cathode layer is in adjacent intimate contact with the electrolyte layer.

Shibata neither discloses nor suggests an anode support layer as recited in claim 12. The base body 1 of Shibata simply cannot be said to correspond to the recited anode support layer since an alumina ceramic is not an oxygen ion-conducting structure. Simply because an alumina ceramic exhibits some ion conductivity does not make such an alumina ceramic an ion-conducting structure. Alumina's resistivity is too high for this material to be considered a solid electrolyte and an oxygen ion conductor for a solid oxide fuel cell and the resistivity is also too high at the operating temperatures to carry out the required electrode function.

For all these reasons, the combination of elements recited in claim 12 is allowable.

During the interview, the Examiner also raised what he termed a potential 35 U.S.C. § 112, paragraph 1, issue regarding the recitation of an ion-conducting structure in the claims and pointed to paragraph 19 of the specification to support his assertion that only a description of oxygen ion conducting materials is contained in the application. See page 3 of the Interview Summary. The Examiner states that "the invention, as presently claimed, may have a [Section] 112 issue (lack of adequate written support, and may be [sic] lack of enablement) because it clearly does not disclose, suggest or teach how "ANY" ion conducting material can be suitably used in the claimed anode structure." While not at issue here a brief reply to this comment is

provided. It is the Examiner and not the Applicant that is inserting the word "any" before the claim term "ion-conducting structure" recited in claims 1 and 12. Claim terms must be construed in the context of the application. As expressly noted by the Examiner on page 3 of the Interview Summary, the present application (paragraph 19, lines 4-7) states "other oxygen ion conducting materials suitable for SOFC use and having a relatively similar thermal coefficient to the electrolyte, as is known in the art, may be substituted for YSZ." Claims 1 and 12 are directed to anode-supported solid oxide fuel cells. In the context of solid oxide fuel cells, one skilled in the art would understand the recited term "ion conducting structure" to relate to oxygen ions. No Section 112 issue exists.

**2. Claims 7-8 and 10 are nonobvious under 35 U.S.C. § 103(a) in view of the combination of Shibata and U.S. Patent Application Publication No. 2002/0028367 to Sammes et al. ("Sammes") since there is no disclosure or suggestion.**

In the final Office Action, the Examiner rejected claims 7, 8 and 10 under 35 U.S.C. § 103(a) as being obvious in view of Shibata and Sammes. As discussed above, nothing in Shibata discloses or suggests the recited anode support layer. Furthermore, Sammes describes anode layers that comprise different ratios of electrochemically active substance. Sammes also describes a process for manufacturing a solid oxide fuel cell anode wherein YSZ powder is added to NiO powder and these materials are milled, extruded, dried and sintered together. As discussed above, one would expect a cross-sectional micrograph of the base body described in Sammes to reveal a porous structure comprising a homogenous composition within each layer. There is no suggestion in Sammes to impregnate catalytic and electronically conductive material into the pores of an anode support layer, thereby creating an anode support layer having a non-homogeneous porous structure.

Claim 7 recites the fuel cell of claim 5 wherein the catalytic and electronically conductive material is Ni-containing material and is compositionally graded through the thickness of the anode support layer, with a higher concentration of the Ni-containing material at one major surface of the anode support layer than the other. The recited

porous structure is non-homogeneous in that the electronically conductive material of nickel Ni is compositionally graded through the thickness of the anode support layer. As a result, the anode support layer has a higher concentration of nickel Ni at one major surface than at the other major surface. Within the recited single anode support layer the electronically graded material is graded through the thickness of this single layer. Sammes discloses multiple layers with the concentration within each layer being homogeneous or constant and not graded. For these reasons, even if combined Shibata and Sammes do not teach or suggest the recited structure of claim 7. Claim 7 is accordingly allowable.

Claim 8 recites the fuel cell of claim 7 wherein the anode support layer further comprises a second conductive metal selected from the group of ferritic steel, super alloy, and Ni-Ag alloy and which is concentrated at the major surface of the anode support layer having the lower concentration of Ni-containing material. Once again, Sammes neither discloses or suggest a single anode support layer having a nickel Ni concentration graded as recited in claim 7 and then a second conductive material concentrated at the major surface of the anode support layer having the lower concentration of nickel Ni as recited in claim 8. Claim 8 is accordingly allowable for these additional reasons.

### **3. Dependent Claims Not Specifically Addressed In Section VIII**

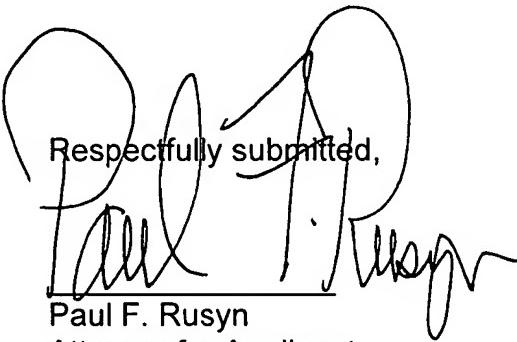
All dependent claims not specifically addressed in this section are patentable by virtue of their respective dependencies from claims for which the Applicants have presented an argument for patentability.

### **IX. Conclusion**

For the foregoing reasons, the Applicants request the Board to reverse the Examiner's rejection of claims 1-6, 9, and 11-12 under 35 U.S.C. § 102(e) and his rejection of claims 7, 8, and 10 under 35 U.S.C. § 103(a) and remand the application to the Examiner for issuance of claims 1-12.

Enclosed is check number 27256 in the amount of \$620.00 to cover the fees associated with filing the Appeal Brief (\$500.00) and the extension of time fee (\$120.00).

Dated: February 8, 2007

  
Respectfully submitted,

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Enclosures:

Appendices A-F  
Request for Extension of Time  
Check #27256 for \$620.00  
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## APPENDIX A

1. An anode-supported solid oxide fuel cell comprising
  - (a) an anode support layer comprising a porous ion-conducting structure having pores impregnated with a catalytic and electronically conductive material;
  - (b) an electrolyte layer in adjacent intimate contact with the anode support layer; and
  - (c) a cathode layer in adjacent intimate contact with the electrolyte layer.
2. The fuel cell of claim 1 wherein the catalytic and electronically conductive material is selected from the group of nickel, copper, silver, tungsten, and any alloys of these materials.
3. The fuel cell of claim 2 further comprising a second phase material mixed with the catalytic and electronically conductive material, the second phase material being selected from the group of yttria-stabilized zirconia (YSZ), doped cerium oxide, alumina or its salts.
4. The fuel cell of claim 2 further comprising an anode functional layer between the anode support layer and the electrolyte layer such that the electrolyte layer is in adjacent intimate contact with the anode functional layer instead of the anode support layer.
5. The fuel cell of claim 4 wherein the porous ion-conducting structure of the anode support layer is substantially yttria-stabilized zirconia (YSZ).

6. The fuel cell of claim 5 wherein the catalytic and electronically conductive material is substantially evenly distributed throughout the anode support layer.
7. The fuel cell of claim 5 wherein the catalytic and electronically conductive material is Ni-containing material and is compositionally graded through the thickness of the anode support layer, with a higher concentration of the Ni-containing material at one major surface of the anode support layer than the other.
8. The fuel cell of claim 7 wherein the anode support layer further comprises a second conductive metal selected from the group of ferritic steel, super alloy, and Ni-Ag alloy and which is concentrated at the major surface of the anode support layer having the lower concentration of Ni-containing material.
9. The fuel cell of claim 4 further comprising a porous zirconia-nickel cermet buffer layer sandwiched in between the anode support layer and anode functional layer, and having a porosity between 40-90%.
10. The fuel cell of claim 4 wherein the porous ion conducting structure of the anode support layer is comprised of a mixture of 10-30 vol. % of Ni, or NiO or both, and the balance yttria-stabilized zirconia (YSZ).
11. The fuel cell of claim 4 wherein the anode support layer further comprises a plurality of vias extending through the thickness of the ion conducting structure of the anode support layer, at least some of the vias being filled with an electronically conducting material.
12. An anode-supported solid oxide fuel cell comprising

- (a) an anode support layer comprising an ion-conducting structure with a plurality of vias extending through the thickness of the oxygen ion-conducting structure, at least some of the vias being filled with electronically conductive material;
  - (b) an anode functional layer in adjacent intimate contact with the anode support layer;
  - (c) an electrolyte layer in adjacent intimate contact with the anode functional layer; and
  - (d) a cathode layer in adjacent intimate contact with the electrolyte layer.
13. An anode-supported solid oxide fuel cell comprising
- (a) an anode support layer;
  - (b) a porous cermet buffer layer in adjacent intimate contact with the anode support layer, and being composed of a zirconia-nickel cermet with a porosity between 40 and 90%;
  - (c) an anode functional layer in adjacent intimate contact with the buffer layer;
  - (d) an electrolyte layer in adjacent intimate contact with the anode functional layer; and
  - (e) a cathode layer in adjacent intimate contact with the electrolyte layer.

*super-  
ionic  
solids*

PRINCIPLES  
AND  
APPLICATIONS

SURESH CHANDRA

*Professor of Physics,  
Banaras Hindu University,  
Varanasi, India*



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## CHAPTER 2

### Superionic Materials and Structures

Superionic solids are ionic materials with high electrical conductivity comparable with those of liquid electrolytes. These materials are also termed "solid electrolytes" or "fast ion conductors". Typically a superionic solid has the following characteristics:

- (i) crystal bonding is ionic;
- (ii) electrical conductivity is high ( $10^{-1} - 10^{-4}$  ohm $^{-1}$  cm $^{-1}$ );
- (iii) principal charge carriers are ions which means that the ionic transference number ( $t_{ion}$ ) is almost equal to 1 (here  $t_{ion}$  refers to the fractional contribution of the ionic conductivity to the total conductivity);
- (iv) the electronic conductivity is small; generally materials with electronic transference number ( $t_e$ ) less than  $10^{-4}$  are considered satisfactory superionic solids.

The values of electrical conductivity of a few ionic and superionic solids are shown in Figure 2.1. The highest conductivity at room temperature obtained so far is for RbAg<sub>4</sub>I<sub>5</sub> which is 0.27 ohm $^{-1}$  cm $^{-1}$ . This is many orders of magnitude higher than those of the more commonly known ionic solids KCl, NaCl etc. which have room temperature conductivity  $\sim 10^{-12} - 10^{-16}$  ohm $^{-1}$  cm $^{-1}$ . It may be noted that most of the superionic materials attain a high electrical conductivity above a certain temperature which may or may not be well defined. In other words, with increasing temperature the electrical conductivity sometimes changes gradually (as in  $\beta$ -alumina) or shows an abrupt jump (e.g. in  $\beta$ -AgI, RbAg<sub>4</sub>I<sub>5</sub> etc.). Furthermore, for the latter materials the abrupt conductivity change is sometimes associated with a distinct structural change (like the  $\beta \rightarrow \alpha$  transition in AgI) but sometimes this is not so clear (as in RbAg<sub>4</sub>I<sub>5</sub>). Structures which allow fast ion transport are generally disordered, "channelled" or "layered" (Wiedersich and Geller 1971). Ion-Ion interactions or correlation

over. Owens (1971) has noted that  $M^+$  ions with volumes greater than  $85 \text{ \AA}^3$  do not generally form conductive compounds. Furthermore, for bigger cations a lesser amount may be needed. For example, the maximum conductivity is obtained with 13 mole % MI for the  $(\text{CH}_3)_4\text{NI}-\text{AgI}$  system; 12.5 mole % in the  $(\text{CH}_3)_2(\text{C}_2\text{H}_5)_2\text{NI}-\text{AgI}$  system and 12 mole % in the  $(\text{C}_2\text{H}_5)_4\text{NI}-\text{AgI}$  system. This means that the percentage of added cations decreases with its increasing size as is expected from Raleigh's picture.

The above structural principles have been deduced on the basis of the very small amount of available structural data — mostly on cation substituted systems. More structural studies would be necessary both on anion and cation substituted systems to arrive at a better understanding.

### 2.8 Oxygen ion conductors

The first solid oxide electrolyte ever used was probably the ceramic with composition 85 wt %  $\text{ZrO}_2$ , 15 wt %  $\text{Y}_2\text{O}_3$  which was used by Nernst (1899) as an incandescent lighting material. Later Baur and Preis (1937) used this material for a fuel cell. The definite conductivity mechanism in terms of oxygen vacancies was proposed by Wagner (1943) and later verified by Hund (1952). However, the sudden increase of scientific interest in such materials started after Kiukola and Wagner (1957a, 1957b) illustrated their use in high-temperature thermodynamic measurements and fuel cells. In principle, almost all oxides can be expected to show some degree of oxygen ion conduction particularly the non-stoichiometric oxides. The non-stoichiometry can be created by heating the metal oxides in vacuum or oxygen or the relevant metallic vapour (Wagner 1974). Most of the oxygen ion conductors are good only at high temperatures ( $\sim 1000^\circ\text{C}$ ) and are mixed conductors (ionic + electronic + electron-hole). As in the case of other ionic conductors, the conductivity in this case is strongly dependent on the temperature and doping with aliovalent impurities (like  $\text{Ca}^{2+}$ ,  $\text{Y}^{3+}$ ,  $\text{Sr}^{2+}$  etc. in  $\text{HfO}_2$ ,  $\text{CeO}_2$  etc.) which control the number of point defects and their mobility. However, a unique property of oxide conductors is the dependence of the conductivity on the ambient pressure or activity. If the ambient oxygen pressure is low, the oxygen ions ( $\text{O}_\text{O}$ ) would leave the solid electrolyte according to the following mechanism:

The defects are expressed in the Kröger-Vink notation: the symbol indicates the defect; the subscript the location of the defect; and the superscripts ('+') denote negative and positive charges respectively. For example,  $V_\text{O}^+$  means vacancy at the oxygen site having effectively two positive charges. Similarly,  $\text{O}_\text{i}^-$  would indicate an oxygen ion at the interstitial site with effectively two negative charges.

tions, cooperative hopping or correlation effects play important roles. Details of the conductivity mechanism will be discussed in Chapter 4. Figure 2.46 gives a schematic plot of conductivity as a function of partial pressure of ambient oxygen for a typical oxide electrolyte at three different temperatures: The higher the temperature, the lower is the range of oxygen pressure over which the conductivity is ionic. The dependence of the range of ionic conduction on concentration of aliovalent dopant (like  $\text{Ca}^{2+}$  or  $\text{Y}^{3+}$ ) is shown in Figure 2.47. The effect of increasing concentration is to broaden the range of ionic conductivity and shift the whole conductivity curve to lower  $p_{\text{O}_2}$  values.

Most of the useful oxide electrolytes developed so far are based on  $\text{ThO}_2$ ,  $\text{CeO}_2$ ,  $\text{HfO}_2$  and zirconia, though some other systems have also been described. For an earlier review see Etsell and Flengas (1970). The common structure which sustains high oxygen ion conduction is the "fluorite structure". The fluorite structure for  $\text{MO}_2$  ( $\text{M}$  = metal ion Th, Ce etc) is shown in Figure 2.48; In this structure there are a large number of octahedral interstitial voids. Each metal cation is surrounded by eight

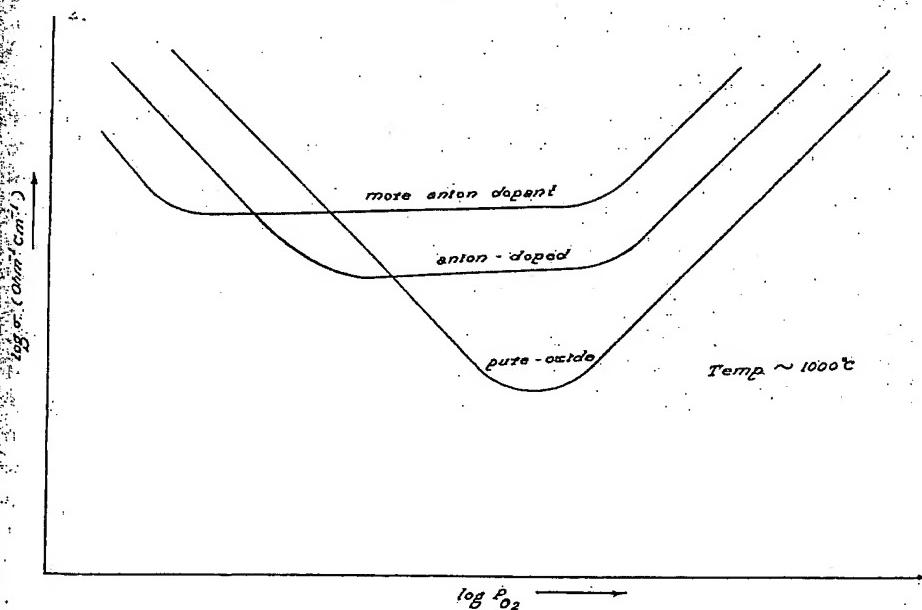


Fig. 2.47 Schematic representation of the dependence of conductivity of any oxide ion electrolyte on oxygen partial pressure for samples doped with different concentrations of aliovalent anion ( $\text{Ca}^{2+}$ ,  $\text{Y}^{3+}$  etc.).

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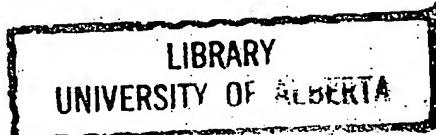
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# MATERIALS SCIENCE AND ENGINEERING HANDBOOK

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## THIRD EDITION

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Division of Materials Science and Engineering  
and  
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## Electrical Properties

**Table 291. RESISTIVITY OF CERAMICS**  
(SHEET 4 OF 6)

Class	Ceramic	Resistivity ( $\Omega\text{-cm}$ )	Temperature Range of Validity
Oxides	Aluminum Oxide ( $\text{Al}_2\text{O}_3$ )	$>10 \times 10^{14}$	25°C
		$2 \times 10^{13}$	100°C
		$1 \times 10^{13}$	300°C
		$6.3 \times 10^{10}$	500°C
		$5.0 \times 10^8$	700°C
		$2 \times 10^6$	1000°C
	Beryllium Oxide (BeO)	$>10^{17}$	25°C
		$>10^{15}$	300°C
		$1-5 \times 10^{15}$	500°C
		$1.5-2 \times 10^{15}$	700°C
		$4-7 \times 10^{15}$	1000°C
	Magnesium Oxide (MgO)	$1.3 \times 10^{15}$	27°C
		$0.2-1 \times 10^8$	1000°C
		$4 \times 10^2$	1727°C
	Silicon Dioxide ( $\text{SiO}_2$ )	$10^{18}$	room temp.
	Zirconium Oxide ( $\text{ZrO}_2$ ) (stabilized)	2300	700°C
		77	1200°C
		9.4	1300°C
		1.6	1700°C
		0.59	2000°C
		0.37	2200°C

Source: Data compiled by J.S. Park from No. 1 Materials Index, Peter T.B. Shaffer, Plenum Press, New York, (1964); Smithells Metals Reference Book, Eric A. Brandes, ed., in association with Ulmer Research Institute Ltd. 6th ed. London, Butterworths, Boston, (1983); and Ceramic Source, American Ceramic Society (1986-1991).

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## insight review articles

# Materials for fuel-cell technologies

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Fuel cells convert chemical energy directly into electrical energy with high efficiency and low emission of pollutants. However, before fuel-cell technology can gain a significant share of the electrical power market, important issues have to be addressed. These issues include optimal choice of fuel, and the development of alternative materials in the fuel-cell stack. Present fuel-cell prototypes often use materials selected more than 25 years ago. Commercialization aspects, including cost and durability, have revealed inadequacies in some of these materials. Here we summarize recent progress in the search and development of innovative alternative materials.

The successful conversion of chemical energy into electrical energy in a primitive fuel cell was first demonstrated over 100 years ago. However, in spite of the attractive system efficiencies and environmental benefits associated with fuel-cell technology, it has proved difficult to develop the early scientific experiments into commercially viable industrial products. These problems have often been associated with the lack of appropriate materials or manufacturing routes that would enable the cost of electricity per kWh to compete with the existing technology, as outlined in a recent survey.<sup>1</sup>

The types of fuel cells under active development are summarized in Fig. 1. The alkaline fuel cell (AFC) and phosphoric-acid fuel cell (PAFC) stacks essentially require relatively pure hydrogen to be supplied to the anode. Accordingly, the use of hydrocarbon or alcohol fuels requires an external fuel processor to be integrated into the system. This item not only increases the complexity and cost of the system, but also reduces the overall efficiency as indicated in Fig. 2. In contrast, molten-carbonate fuel cells (MCFC) and solid-oxide fuel cells (SOFC) operate at higher temperatures have the advantage that both CO and H<sub>2</sub> can be electrochemically oxidized at the anode. Moreover, fuel-processing reaction can be accomplished within the stack, which enables innovative thermal integration/handling, design features to provide excellent system efficiencies (>55%).

Although the introduction of a 'hydrogen economy' might seem an attractive scenario, its implementation is faced with formidable technical and economic difficulties. The cheapest technology for the large-scale production of hydrogen is the steam reforming of natural gas, which produces significant emissions of greenhouse gases.<sup>2</sup> The topic of hydrogen storage is discussed in the accompanying review by Schlapbach and Zuttyl (see page 56–59). Indeed there is a breakthrough in the production of hydrogen and the development of new hydrogen-storage materials, the concept of a hydrogen economy will remain an unlikely scenario. In this article, therefore, we assume that fuel cells have to be designed for operation on hydrocarbon or alcohol fuels to ensure that the technology is able to penetrate the relevant major markets. Otherwise fuel-cell technology will be confined to retailed niche applications where hydrogen might be a commercial option, such as city bus fleets. Clearly the choice of fuel is a

further complication in the factors influencing the commercialization of fuel cells.

### Constraints on material selection

Materials selection for a commercial product involves an iterative design process that eventually becomes specific to the particular product and application. However, it is possible to make a few general statements about the selection of materials for fuel cells. The cathode and anode resistivity (ASR) of these cell components (electrode, anode and cathode) should be below 0.5 Ω cm (ideally approach 0.1 Ω cm) to ensure high power densities, with targets of 1 kW dm<sup>-2</sup> and 1 kW kg<sup>-2</sup> often mentioned for 'transport applications'. High power densities are also important to reduce costs as the amount of cell components is minimized. These topics, and considerations of cell efficiencies, are summarized in later sections. The need to minimize cell resistivity has a major impact on the selection and processing of the cell components. Cost-effective fuel-cell proton-conducting structures was achieved for the first time only about 40 years ago. The electrolyte, gaseous reactants, electrolyst and current collector have to be brought into close contact within a confined spatial region termed the triple-phase-heterogeneity interface. For the low-temperature systems, the introduction of hydrophobic polytetrafluoroethylene (PTFE or Teflon) greatly simplified the fabrication of porous, liquid-tight gas-diffusion structures. Metal or carbon pores (or porous carbon paper) provided the electronic pathways and to interconnect the electrodes and the anode with the cathode screen was usually incorporated into the structure. Further improvements in performance were obtained during the 1990s by depositing small crystallites (2–5 nm) of the electrolysts (usually platinum or Pt alloy) onto carbon powder or paper. In retrospect, this accomplishment was probably the first manifestation of an engineered nanostructure, and it is not surprising that its implementation took over 10 years to go from scientific to practical.

High-rate conductivities (>1 S cm<sup>-1</sup>) associated with the liquid KOH, phosphoric acid and molten carbonate electrolytes ensured that, with appropriate design strategies, the ASR values of these components can be small. Although exhibiting lower specific ionic conductivity values, the Nafion membrane used in the PEMFC system can be fabricated relatively easily as a thick film (100 μm) to produce satisfactory ASR values, provided the water content of the film is controlled under the dynamic conditions of cell operation. In contrast, it has been, and continues to be,

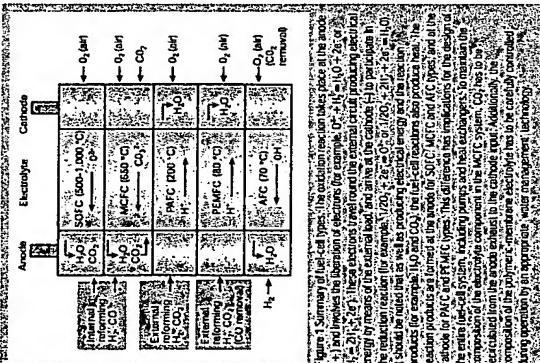
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Page: 1

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Additional constraints influencing material selection arise from additional durability and durability issues. For transport applications, minimal rates of performance degradation (for example, 0.1% over 1,000 h) are required for projected operational lifetimes of 5 years. For aerospace applications—for example, distributed CHP (controlled heat and power systems)—a similar degradation rate must extend over a period of at least 10,000 h (5 years). These different lifetime requirements seem to be introducing problems for PEM prototype CHP systems, if the solid-state components were developed originally for transport applications.

Anchored polyimide incorporates relevant features of plantarums or anchorage points such as punch, valves, heat exchangers and piping. Although these component components constitute at least half the cost of a fuel-cell system, we will not consider them further here, except to note that for a fuel-cell system approaching 50,000 h, the main source of system lifetime has been shown to be the proton-exchange-polymer membrane.

External parts (process reformers) are also subject of intensive development around the world, and a variety of alternative compacted materials using diffusion-barrier printed-circuit technology have been developed, also illustrating the impact of the fuel-cell system.

For more than four decades now, fuel-cell researchers, fuel-cell developers, and fuel-cell technology experts have proved their worth in the Apollo programme and space shuttles. External electrodes, kinetics, when operating on pure hydrogen and oxygen, are an attractive feature of its system. But for terrestrial applications, the additional economic factors of installation, which include the need to replace hydrogen by cheaper hydrocarbons or alcohol fuel, have provided severe problems for plantarum selection and the associated fuel-processing technology.

difficult to scale-up thick-film technologies to provide cost-effective ceramic solid-codelectric components with required thicknesses in the range 1–10 µm. Ideally the thick-film electrolyte has to be sintered dense at temperatures approaching 1,400 °C; this requires a porous ceramic substrate. Which is often the anodic or cathode material [1]. The ceramic material has to be carefully selected to avoid reaction with the electrolyte, and/or thermal expansion mismatch, during the high-temperature sintering process. The incorporation of a relatively weak, brittle structural component in SOFC stacks is at present hindering the application of SOFC systems to their full potential due to demanding stack temperature fluctuations. In this respect the recent development of sintering procedures below 1,000 °C, which should allow the use of metal substrates, represents a significant advance that

will enable the development of more rugged SOFC systems. Another important component in a fuel cell is the impermeable electrically-conducting bipolar plate. This has the dual function of distributing the fuel and air to the anode and cathode, respectively, as well providing the electrical contact between adjacent cells. The constraints on the materials prevailing in the PEMFC and PAFC systems severely restricts the choice of bipolar plate material and at present graphite is usually selected. However, alternative materials or manufacturing methods are mandatory if these systems are ever to attain the target costs. Major research and development (R&D) programmes are examining the behaviour of alternative carbon-based materials produced by injection moulding, or coated stainless steels. For the high-temperature systems (MFC and SOFC) operating in the temperature range 500–750 °C, appropriate stainless steel compacts can be specified with SOFCs operating at higher temperatures (900–1000 °C), alternative, more expensive bipolar plate materials have to be employed, which present significant cost penalties.

60% efficiency produced by injection molding, or oriented stainless steel.

For the high-temperature extremes (MWCOT and SOFC) operating in the temperature range 500–750 °C, appropriate stainless steel compositions can be specified which simultaneously satisfy the technical and economic constraints. But for SOFCs operating at higher temperatures (1000–1000 °C), alternative, more expensive bipolar plate materials have to be specified, which will incur significant cost penalties.

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Approximately 100 PAFC co-generation units (international fuel cells) PC25 systems, delivering 200 kW have been installed throughout the world, and have exhibited excellent reliability. However, as a commercial failure of this system is possible in the long term, the manufacturers (IEC and Japanese companies) have been unable to reduce the capital cost significantly below US\$33,000 per kW, as originally forecast.<sup>1</sup> Most observers<sup>2</sup> believe that for India market initially the target cost per kW, must be reduced to around US\$11,000 per kW, failing to reach US\$10,000 per kW by volume production. Economically, we focus here on materials aspects of the PEMFC, SOFC and SORC systems, which at present still appear to present opportunities to exploit the potential.

It is important to note that the materials currently being used in PAFC, MCFC and tubular SOFC prototype demonstration units remain the same as those selected at least 25 years ago.<sup>3</sup> Although many innovative development and processing routes have been developed, the attributes (for example, lower cost and lower Pt loading) of these materials are not known in the fast moving field that system engineering and commercialisation issues have highlighted the need for some of the materials originally selected. As indicated in the next two sections, all these issues are now driving the development of alternative materials, particularly for the PEMFC and intermediate temperature (IT)-SOFC stacks.

### Polymer-electrolyte-membrane fuel cells

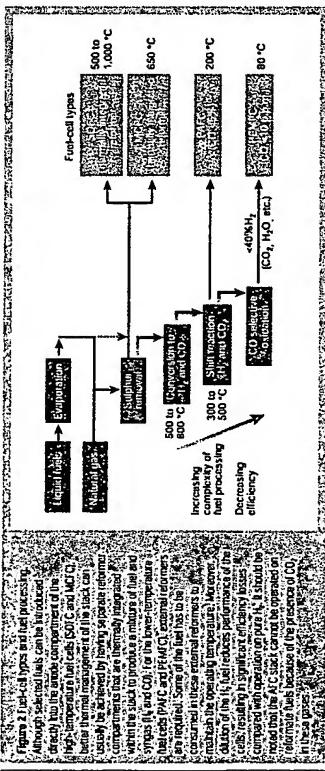
The most important materials under development for PEMFC stacks are construction materials for the cell frames, bipolar plates, interconnects, and membrane electrolysis systems for the fuel and air electrode, and the conducting polymer.

Depending on the fuel to be used in the PEM cell, the requirements for these materials are completely different. The simplest case is the use of pure hydrogen and oxygen. Cells with high

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## insight review articles

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power density and very low degradation are already state of the art. The main requirement for the future is to achieve reduction in the capital cost of the system by attention to material selection and fabrication, and also by scaling-up the production volume. This target will probably cause a complete review of all the materials used up to now. The second possibility is to operate the PEM cell with a reformate fuel. In that case, inert gases and CO traces are present in the fuel. This is a challenge for the fuel electrode in particular, and a CO-tolerant catalyst is required. The most difficult option is the direct methanol fuel cell (DMFC). The methanol electrode also needs a CO-tolerant catalyst, as adsorbed CO species are formed during the electro-oxidation of methanol. In addition, the small polar methanol molecule behaves in a way similar to water and readily permeates through existing membrane materials. This behaviour leads to a loss in fuel and also to the formation of a mixed potential at the air electrode. The development of innovative membrane materials could remove this disadvantage. As the tolerance to CO by the electrolysis is strongly dependent on temperature, an alternative membrane with a better temperature stability is also another

important R&D target. However, an operation temperature above the boiling point of water requires a completely different type of membrane material, as no liquid water will be present under these circumstances for the hydrated protonic-conduction mechanism.

### Bipolar plates

Much effort is being expended on the development of cost-effective materials for the bipolar plates. However, the conductivity of graphite materials is much less than that of metallic materials. Some conductivity values are: C polymers,  $\sim 1.5 \text{ S cm}^{-1}$ ; graphite,  $10.5 \text{ S cm}^{-1}$ ; gold,  $15,000 \times 10^3 \text{ S cm}^{-1}$ ; Fe alloys,  $5,300 \times 10^3 \text{ S cm}^{-1}$ ; Ti,  $12,400 \times 10^3 \text{ S cm}^{-1}$ . For bipolar plates, polymer/graphite compounds are developed with at least  $0.5 \text{ S cm}^{-1}$ , reducing the resistivity of the bipolar plate well below the resistivity of the membrane. In addition, the fabrication costs of graphite plates incorporating gas-distribution channels are high, making such components too expensive. Moreover, as graphite materials are porous, a binder or resin has to be added to produce the necessary impermeability.

Polymeric materials can be machined more easily and cheaply by hot pressing or injection moulding. Polypropylene, for example, can be mixed with graphite to achieve sufficient electrical conductivity values, but the associated mechanical properties become undesirable as the increased brittleness not only reduces the toughness, but also makes manufacturing more difficult and expensive. Typical carbon contents range between 30 and 80 weight%, and several groups<sup>14,15</sup> are optimizing the machining processes in association with optimization of the material.

Another strategy to use metallic bipolar plates. The gaseous flow structure can easily be fabricated in thin metal foils by pressing, but only a few metals are sufficiently corrosion-resistant in the acidic environment of the membrane. The most promising metals are stainless steels, as the other candidate metals such as titanium, niobium, tantalum and gold (including gold-plated metals) are too expensive. Stainless steels can provide satisfactory performance for several thousand hours. The steel is protected by a passive layer at the cathode side, but the anode side becomes contaminated by corrosion products<sup>16</sup>. Stacks with metallic bipolar plates have been developed by Novea and by Siemens.

**Electrocatalyst**  
The second important problem is associated with the electrocatalyst. For operation with pure hydrogen and air, platinum is the most active material. To reduce the cost, nanoparticles of platinum on a carbon

substrate are used. The overall cell efficiency  $\eta$  is given by the equation

$$\eta = \eta_{\text{v}} \eta_{\text{a}} \eta_{\text{c}}$$

where  $\eta_{\text{v}}$  is the cell voltage efficiency,  $\eta_{\text{a}}$  is the anode efficiency and  $\eta_{\text{c}}$  is the fraction of fuel used.

$$\eta_{\text{v}} = A(\Delta V - iR_{\text{v}})/\Delta H$$

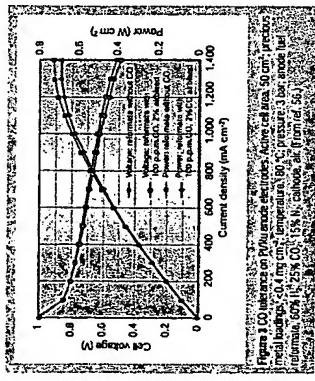
$$\eta_{\text{a}} = E/E_{\text{a}} = (E_0 - iR_{\text{a}})/E_0$$

where  $E_0$  is the open circuit voltage, and  $\Delta H$  is the heat of the overall cell reaction. Thus

$$\eta = A(E_0 - iR_{\text{a}})/\Delta H$$

$R_{\text{v}}$  is the area specific resistance of the cell components (electrode, anode and cathode). Note that the cell structure is often termed the membrane-electrode assembly (MEA) for PEMCs systems, and positive-electrode-negative (PEN) for SOFC systems.

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mechanical permeability, and stability — and the type of backbone polymer, the degree of sulfonation and the name phase separation into hydrophilic and hydrophobic domains (for example, high degrees of sulfonation usually lead to highly conductive membranes, but are to extremes swelling properties). To satisfy these requirements, different approaches have been pursued: sulfonated PEI-polymerized with, and without, micropositional support; sulfonated polyetheroxides; acid-base complex and composite materials with improved thermal stability and better water-retaining properties.

Because of their PTFE-like backbone and relatively low equivalent weight, halogen and related materials are a favoured option and are commonly used. In fact, PTFE, but also the cast variants, high-TEFPE, often fluorine-free membrane materials, but also hydrocarbons often suffer from an insufficient thermal stability, and so more and more aromatic groups have been introduced into the polymer backbone. Poly(arylene sulfone)s seem to be the most stable molecules among the hydrocarbons. For example, poly(arylene ether sulfone)-based membranes were prepared by sulfonation of poly(ether sulfone)-based polyimides such as *Tiegel* and *Nerac*.<sup>20</sup> Far higher ion conductivity, high sulfonation fractions are definable, but high sulfonation can lead to extreme swelling even at room temperature. Thus, crosslinking of the polymer chains at the sulfonic acid groups can be included in the synthesis steps to overcome the problems of swelling. However, the long-term stability of these sulfonamido crosslinking bridges remains unproven. Alternative crosslinking methods such as covalent crosslinking and ionic crosslinking by the introduction of polymeric acid-base binders, however, have

support have been developed, and the reduction in noble-metal content without degrading the cell performance has been, and continues to be, an important R&D activity.<sup>10</sup> The platinum loading has been significantly reduced from 2 mg per square centimetre of electrode to values below 0.5 mg cm<sup>-2</sup>, without significant impact on performance and lifetime. In the laboratory, even lower platinum loadings have been examined.<sup>11</sup>

For fuels containing traces of CO, or methanol in the DMFC, a Cu-Tollen catalyst is required. This remains one of the most challenging tasks for the successful development of commercial DMFC systems.<sup>12</sup> For reformate electrodes as well as for methanol oxidation, the removal of adsorbed species is the rate-determining step. The oxidation of adsorbed CO on Pt is slow, and it is facilitated by adjacent absorbed OH species. This is the reason why, with low potential for OH-ads formation, is the most efficient component of the binary catalysts, Pt/Ru, and other binary and ternary alloys with these noble metals have been investigated intensively,<sup>13</sup> and performance values have increased significantly. The loss in performance is usually expressed in mV for a certain CO content of the fuel, and recent publications show promising results, as indicated for example, in Fig. 3.

**Membranes** Although the US General Electric Company (GE) initiated the development of PEMFCs in the 1950s, it was the introduction of Nafion by DuPont that ensured continuing interest in these systems. Initially Nafion was manufactured<sup>4</sup> for membrane cells used in the production of chlorine (chlor-alkali cells). By 1950, Ballard had overcome many of the engineering problems associated with PEMFC systems, and this had stimulated many groups in the United States and Japan to improve the properties of the original Nafion model 101<sup>5</sup>. For example, higher ionic conductivities could be attained by selecting perfluorosulfonic acid copolymers with a short pendant group, and it was realized that gas and small-molecule permeability were other important characteristics that had to be improved.

The following properties of polymeric membranes need to be optimized for use in fuelcells: (1) high proton conduction, assured by acid lone groups (usually SO<sub>3</sub><sup>-</sup>), depending on a sulfonation degree and on the thickness of the membrane; (2) good mechanical and thermal strength requiring the selection of a suitable polymer backbone; mechanical strength for thin membranes can frequently be improved by reinforcement; (3) low gas permeability, which is dependent on material and thickness of the membrane; (4) for DMC applications low electro-kinetic drag coefficient to reduce methanol crossover.

There is significant interaction between the desired properties of the membrane — high conductivity, low swelling, low gas and

Fuel cells operating at elevated temperatures

Solid-oxide fuel cells

In contrast to other fuel-cell types a SOFC stack can, in principle, be

designed to operate within a wide temperature range (300–1,000°C).

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### Fuel cells operating at elevated temperatures

Solid-oxide fuel cells

In contrast to other fuel-cell types a SOFC stack can

It is apparent that few, if any, the isolated designs can operate within a wide temperature range.

THE JOURNAL OF CLIMATE

of the properties of available solid electrolytes.

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NATURE | VOL 314 | 15 NOVEMBER 2001

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If the SORC block is to be integrated with a gas turbine, then system requirements indicate that the retemperature of the exhaust gas from the block should exceed about 850°C. The steam reformation of methane, which is used as fuel, produces hydrogen and CO gases for the combustor; as present, requires the processors operating at temperatures of up to 700°C. But it is the specific heat conductivity of a material that determines the biggest influence on stack design and material selection, as figure 4 summarizes.

selection of solid electrolytes works with the reciprocal of temperature. By taking a typical value of  $15 \text{ J/m}^2\text{K}$  for the maximum ASK available, it is feasible to calculate the maximum thickness allowed for a given volume of electrolyte component. For example, a design configuration specified a self-supported ( $\sim 50 \text{ } \mu\text{m}$ ) yttria-doped zirconia electrolyte with a square cross-section of  $1 \text{ cm} \times 1 \text{ cm}$ , paces major limitations for planar  $\text{Si}/\text{SiO}_2/\text{Si}$  operation at  $1500^\circ\text{C}$ . Operation at a temperature of operation greater than  $1500^\circ\text{C}$  would require a much thicker electrolyte layer.

In most cases, the deposition of the  $\text{La}_x\text{Si}_y$  film was not successful. This arrangement uses 1.5–1 mm long tubular cathodes. After deposition of the  $\text{La}_x\text{Si}_y$  film, the substrate temperature is about 100 °C. After deposition of the  $\text{La}_x\text{Si}_y$  film, the substrate temperature is about 100 °C.

**Fig. 1.** Specific conductance of the polymer film plotted against temperature for different electrode spacings. The film was produced using the conventional ceramic vibration method. The film thickness was about 15  $\mu\text{m}$ . A table that lists the specific conductance of the film at different temperatures for different electrode spacings is given in Table I. It can be seen that the conductivity of the film is increased with increasing temperature. This is also evident in Fig. 1. The conductivity of the film is increased with increasing temperature, and it is also evident that the conductivity of the film is increased with increasing electrode spacing.

**Fig. 2.** Specific conductance of the polymer film plotted against temperature for different electrode spacings. The film was produced using the conventional ceramic vibration method. The film thickness was about 15  $\mu\text{m}$ . A table that lists the specific conductance of the film at different temperatures for different electrode spacings is given in Table I. It can be seen that the conductivity of the film is increased with increasing temperature. This is also evident in Fig. 1. The conductivity of the film is increased with increasing temperature, and it is also evident that the conductivity of the film is increased with increasing electrode spacing.

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The significant reaction between the LSM cathode and electrolyte, which limits the selection of the cathode (LSM) and anode ( $\text{Ni}(\text{YSZ})$ ) compositions, was established during the 1970s and 1980s, after which a variety of cathode compositions for long-term compatibility with YSZ at elevated temperatures. This has been largely explained in terms of a ~~wide interfacial contact~~<sup>interfacial reaction</sup> between the LSM cathode and electrolyte.<sup>1</sup>

That is, a strategic programme of large multinational companies (such as Westinghouse, GE, and ABB) favoured the development of multi-temperature, multi-pressure, high-temperature SFRG stacks, and thus utilities had a choice of SFRG designs and materials to choose from. It was beginning to be recognized that for smaller SFRG stacks not suited to integrated systems, the operating temperature should be lower, as far as possible without compromising the electrokinetic and internal resistance of the cell. The development of the small, ITI STAND-By units for distributed (unended) CHP units to implement a deregulated electricity and gas supply policy. In addition, many automotive manufacturers are examining whether small SFRG stacks (3–5 kW) can be used to supply the electrical power for auxiliary functions such as air conditioning in vehicles.

Examples of the most biocompatible  $\text{SOI}$ -like materials are  $\text{SiO}_2$ -doped  $\text{SiN}_x$  composites [50, 51] and  $\text{SiO}_2$ -doped  $\text{Si}_3\text{N}_4$  composites [52]. The  $\text{SiO}_2$  addition has the two-fold advantage of increasing the thermal expansion coefficient and that the  $\text{SiO}_2$  is biologically inert. In addition, it does not contribute more than 0.15 fm to the total atom  $\text{ASV}$ , which is the sum of the atomic  $\text{ASV}$  of the individual atoms in the material. For a film thickness of 15  $\mu\text{m}$ , the associated specific ionic conductance ( $\sigma$ ) of the insulator should exceed  $1 \times 10^{-5} \text{ S cm}^{-1}$ . The ionic conductance of  $\text{SiO}_2$  at  $T = 0.01 \text{ K}$  is  $10^{-15} \text{ S cm}^{-1}$ . The combination of Fig. 4 indicates that the ionic conductance of  $\text{YSZ}$  at  $T = 0.01 \text{ K}$  is the largest value around  $700 \text{ pS}$ . The use of a thinner dielectric film would allow the operating temperature to be increased. But, as present, it seems that the minimum thickness for dense impermeable films that can be reliably mass produced using a relatively slow ceramic fabrication route is around 10–15  $\mu\text{m}$ . This is due to the fact that the  $\text{YSZ}/\text{SiO}_2/\text{YSZ}$  system is composed of three layers of different materials with different mechanical and structural arrangements, which is difficult to support on an appropriate substrate. As the substrate is to be used in a  $\text{SOFC}$  configuration that selects to retain the specific advantages of floating tubular and planar arrangements, a design developed by the British company Srujan-Royce<sup>1</sup>. This integrated planar-tube concept incorporates a multi-cell assemblies connected in series and supported by a ceramic substrate, and has many similar features to the original Westinghouse<sup>2</sup> monolithic design.<sup>3</sup>

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Page: 5

This strategic programme of large multinational companies (such as Westinghouse, GE, and ABB) favoured the development of multi-terminal, high-temperature, SOFC stacks, and it has furthered their lead, having a significant influence on the development of SOFCs' design and materials over the last two decades from 1970. By 1985, however, it was beginning to become apparent that for smaller SOFC stacks not included in the integrated powerplants built until then, the operating temperatures should be lowered as far as possible without compromising the electrode kinetics and thermal resistance of the cell. The development of these smaller (1 SOFC unit) systems, key for distributed (unified) CHP units, to produce stand-alone electricity generation, is also being stimulated by liberalization (regulation) of local utility supply policies. In addition, many automotive manufacturers are examining whether small SOFC stacks (3–5 kW) can be used as air conditioning in vehicles.

Examples of the most appropriate solid-electrolyte composition for SOFC operation at intermediate temperatures (500–750 °C) include  $\text{K}_{0.8}\text{Na}_{0.2}\text{Zr}_{0.15}\text{Ti}_{0.85}\text{O}_3$  (ZST), which has the characteristic feature of a low ionic conductivity ( $0.01 \text{ S cm}^{-1}$  at 700 °C) and a high mechanical strength. The introduction of ZST into a thick-film stack (Fig. 4) indicates that the ionic conductivity of ZST attains its target value around 700 °C, and the ionic conductivity of the thin-film electrolyte is about 10<sup>3</sup> times higher than that of the cathode. The minimum operating temperature to be lowered. But at present, it seems that the minimum temperature for dense, impermeable films that can be reliably mass produced and handled safely (without ceramic lamination routes) is around 1000–1100 °C. This is due to the fact that the  $\text{Li}-\text{Al}_2\text{O}_3$  glassy electrolyte requires an appropriate substrate. As the substrate is the anode, it is necessary to take into account the conflicting requirements of mechanical strength and dimensional stability.

An SOFC configuration that seeks to retain the specific advantages of the solid-state and planar arrangements is being developed by the Japanese company "Fuel Cells-Royal". This integrated planar–stack concept incorporates the advantages of both cell and stack assemblies connected in series and supported by ceramic substrates, and has many similarities to the original Washington industrial design.<sup>12</sup>

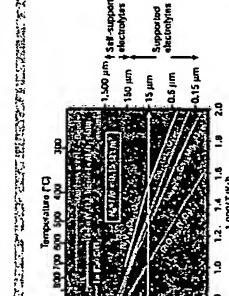
Most development work on planar (1 SOFC) systems has involved thick-film (TC) electrolytes, and so far most groups have used anodized  $\text{Al}_2\text{O}_3$  substrates, which allow the electrolyte powder to be absorbed onto the surface to a depth of 1–100 µm. One of the problems associated with using such porous, composite  $\text{Na}_2\text{SO}_4$  substrates is their relatively poor mechanical strength, and therefore compatibility with the YSZ thick film.

Consequently, several groups are examining porous substrates based on  $\text{Al}_2\text{O}_3$  (or  $\text{MgO}$ ) incorporating  $\text{Na}_2\text{SO}_4$  anular doped  $\text{Co}_2\text{O}_4$ . Although the epitaxial growth of YSZ can provide better thermal expansion compatibility, problems still remain over the volume changes associated with the

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The Stornoway-Westinghouse cell has been enhanced in this regard by the use of a tubular design, which has been developed to reduce the reaction between the LSM cathode and electrolyte. The Stornoway-Westinghouse cell has been enhanced in this regard by the use of a tubular design, which has been developed to reduce the reaction between the LSM cathode and electrolyte. The Stornoway-Westinghouse cell has been enhanced in this regard by the use of a tubular design, which has been developed to reduce the reaction between the LSM cathode and electrolyte.

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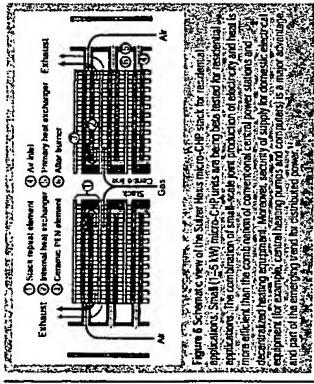


Figure 5. Schematic view of the Stork-Hewitt-Brown (SHB) stack. Micro-channels are being developed for residential applications and small ( $1\text{--}5\text{ kW}$ ) micro-fuel cells are being tested for residential applications. The combination of small-scale fuel production and electricity generation will have a more significant effect than the combination of conventional power stations and fuel production. Micro-fuel cells will be able to supply power to individual houses and buildings.

with the reduction and oxidation of the Ni component. As the porous substrate-electrolyte films are usually co-fired in air at around  $1,400^\circ\text{C}$ , nickel is present in NiO, which has to be reduced to Ni in fuel during the initial heating cycle of the assembled stack. Additionally, operating temperatures have to be kept low to prevent the risk of melting when SOFC stacks are cooled down in the absence of fuel flow, through the anode compartment. (In this case there is the use of a turning gear,  $\text{Ni}_3\text{Al}$ , to protect the Ni-YSZ anode in the Shattock-Watkinson tubular configuration). Most Ti-SOFC development is using anodic interlayer plates. Often afterburner stabilities need specific thermal treatments (e.g.  $12.5 \times 10^7\text{ K}^\text{2}$ ) to permit sealing requirements of these alloys. Moreover, by using contacts stabilized with Ni-Ti, excellent electrical interfaces can be maintained between the cell components for extended periods. Providing appropriate pre-treatments are followed many R&D laboratories have reported good performance values for Ti-SOFC stacks incorporating the following positive-electricity-negative (PEN) components: anode-supported thick-film YSZ electrolytes, LSM-YSZ cathodes, and stainless steel bipolar plates.

To minimize sealing requirements, many Ti-SOFC stacks have adopted a circular design in which the fuel and air are introduced by means of an annular manifold at the centre of the PIN structure. Arrangements are made to distribute the air and fuel gases over the cathode and anode, and the nozzles are adjusted to ensure almost complete conversion of the fuel by the flame. It reaches the stack periphery. Unreacted fuel and air are then combusted without large temperature changes. These design features minimize scaling problems and allow limited thermal cycling. Examples are provided by the Sulzer stacks in their CHP configuration designed for residential accommodation (Fig. 5) and the auxiliary power unit (APU) prototype (Fig. 6), manufactured by the Delft Institute of Chemical Thermodynamic research group for incorporation into vehicles (Fig. 7). Thermo-kinetic reasons limit its incorporation into vehicles, but at present the heating and cooling rates cannot exceed  $-500^\circ\text{C}/\text{min}$ , owing to the development of stresses associated with thermal expansion mismatch, and to the brittle glass and ceramic seals. Although this restriction may not be so severe for larger CHP systems ( $>10\text{ kW}$ ), it is not satisfactory for smaller systems ( $1\text{--}10\text{ kW}$ ) designed for micro-CHP and APU applications. Further R&D is still required to produce more rugged Ti-SOFC stacks. Commercial units can be expected in the next five years at costs of  $\text{US\$1,000}$  per kW (Table 1).

Although YSZ is still the favoured electrolyte material for SOFC stacks, selection of this material is not without problems and research

continues into the long-term evaluation of strontium-doped  $\text{ZrO}_2$ .

In principle, the use of ceria-based electrolytes such as CGO should allow the operating temperature to be lowered to around  $500^\circ\text{C}$  (see Fig. 4). But perched problems associated with PIN structures incorporating ceria-based electrolytes have restricted investment in this technology. It is well known that, at elevated temperatures,  $\text{Ca}^{+2}$  ions can be reduced to  $\text{Ca}^{+1}$  under fuel-rich conditions, degrading the efficiency and performance of cells. However, if the operating temperature is lowered to around  $500^\circ\text{C}$ , then the electronic conductivity is small, and oxygen negates under typical operating conditions of the cell<sup>44</sup>.

Anodized yttria-stabilized zirconia (YSZ) has attracted exploitation of the attractive properties of CGO at  $500^\circ\text{C}$  (for example,  $0.5\text{ V at }1\text{ A cm}^{-2}$ ). Anodized YSZ has been used to fabricate alternative anode compositions that function effectively at lower temperatures. Recent developments in this area have been surveyed by Itoh *et al.*<sup>45</sup>, and there are implications<sup>46</sup> that appropriate materials or composite cathodes can be fabricated which exhibit low overpotentials at  $500^\circ\text{C}$  (for example,  $0.15\text{ V at }1\text{ A cm}^{-2}$ ). CGO anodes, such as  $\text{NiCrGa}_2$ , also provide adequate performance at  $500^\circ\text{C}$  for simulated syngas fuels, indicating that Ti-SOFC stacks are feasible<sup>47</sup>. Careful optimization, utilizing that operation at intermediate temperatures, is initiating a R&D effort into alternative anode compositions to replace the established Ni-YSZ anode. One strategy is to develop electronic structures that are relatively stable, to avoid the loss of Ni. This metal can entrap carbon deposition under certain operating conditions, and thus forms NiO, which is accompanied by a deleterious volume expansion, when the anode compartment becomes hot oxidizing<sup>48</sup>. Another approach is concerned with the identification of a ferritic anode that allows the diffusion of hydrocarbons<sup>49</sup>. The claims made in recent publications are, however, remain controversial<sup>50</sup>. There is little doubt that this topic will remain a fruitful area for further investigation.

Operation at  $500^\circ\text{C}$  allows the use of compliant high-temperature gaskets in place of rigid, brittle glass or ceramic seals, thus permitting greater design flexibility for the stack configuration. At Imperial College, London, researchers have taken advantage of the fact that the thermal-expansion coefficient of CGO and ferritic steels are virtually identical ( $12.2 \times 10^{-6}\text{ K}^{-1}$ ), so that the ferritic-anode structure can be supported on a porous stainless steel foil. These trials supported NiO structures are robust, and should withstand the rapid temperature cycles expected during operation of small Ti-SOFC stacks.

Another electrolyte, doped  $\text{La}_2\text{O}_3$  (LSCM), is also attracting much attention for Ti-SOFC applications. Although its conductivity is slightly smaller (see Fig. 1) than CGO at  $500^\circ\text{C}$ , its ionic current is wider and it could be more appropriate to use this electrolyte at temperatures above  $600^\circ\text{C}$ , where the reduction of  $\text{La}_2\text{O}_3/\text{La}_{2-\delta}\text{O}_{\delta}$  becomes significant. It has been difficult to fabricate pure single-phase ceramic electrolytes, and second phases such as  $\text{SrLa}_2\text{O}_4$  and  $\text{La}_2\text{O}_3$  are often detected in the grain boundaries. Whether these phases are responsible for the enhanced reactivity of LSM, or whether it is an intrinsic property of LSM, are questions that require urgent answers. Moreover, the preferred composition,  $\text{La}_{1-x}\text{Sr}_x\text{O}_{2-\delta}$ , due to its stable intermediate structure (2.5 mol % Sr), is perhaps a constraint. Although research continues into synthesis of alternative oxygen-ion conducting electrolytes, it has proved difficult to prepare alternative materials with an appropriate combination of properties that can displace the traditional fluorite compositions involving  $\text{ZrO}_2$  and  $\text{CeO}_2$ .

Experiments involving single-compartment SOFC fuel cells have been reported. In this configuration a mixture of the fuel and air flows

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167 *Environ Monit Assess* (2008) 146–167

part-load performance. This, for example, is the strategy adopted recently by the US Department of Energy for the Solid-State Energy Conversion Alliance, which aims to mass produce 1 MW SOFC modules at a cost with a target cost of US\$400 per kW. Once the small-scale technology has demonstrated its reliability, and net costs are lower, then larger units built on the same technology can be expected to penetrate other sectors of the stationary power and transport market.

Another area receiving increased attention is the development of portable electronic devices. As fuel-cell power sources for a variety of portable electronic devices, batteries struggle to keep up with the specific power demands of mobile devices. Innovative DMFC designs,<sup>1</sup> fabricated using technologies developed for the semiconductor industry, promise energy densities that are between three and five times better than current



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**Table 1** Materials used in the MCFC stack

Material	Description	Supplier
Anode	NiCr alloy (Ni 50% Cr 50%)	U.S. Smelting Refining Co.
Cathode	NiCr alloy (Ni 50% Cr 50%)	U.S. Smelting Refining Co.
Electrolyte	Lanthanum carbonate (LaCO <sub>3</sub> )	U.S. Smelting Refining Co.
Membrane	Sintered stainless steel	U.S. Smelting Refining Co.
Spacer plate	Stainless steel 316L	U.S. Smelting Refining Co.
Flange	Stainless steel 316L	U.S. Smelting Refining Co.
Was. seal	Graphite	U.S. Smelting Refining Co.
Maintained chamber	Stainless steel 316L	U.S. Smelting Refining Co.
For electrode immobilization	Stainless steel 316L	U.S. Smelting Refining Co.

kg

m<sup>2</sup>

kg

</div

Spar Plug use alumina since it is electrically insulator:

<http://yshsp.en.alibaba.com/search/offer>

Auto Ignition System use alumina since it is an insulator:

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<http://www.ortechceramics.com/alumina.htm>

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Alumina use in thermocouple assembly as a insulator:

### PDF] Noble Metal

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elements, elements with **insulators** or assemblies. A typical. assembly includes a head, **alumina insulators** and a protecting ...

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Page 8 -shows use of alumina tube in an assembly as a insulator:

### Henry Rohrs poster

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**Alumina Insulator.** Nickel Seat. Gold O-Ring. SS O-Ring Seat. Vespel Support. Sapphire Ball. PZT Bimorph. Pulsed Valve. The pulsed valve consists of a ...

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Goodfellow- a table listing volume resistivity of alumina  $>10^{14}$  ohm-cm.:

[http://www\\_azom\\_com/details.asp?ArticleID=2103](http://www_azom_com/details.asp?ArticleID=2103)

## APPENDIX F

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